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Thermal behaviour of the normal surface of Egyptian Kaolinite*

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This investigation was carried out on Egyptian kaolinite clay obtained from Mosabba Salama in Sinai Peninsula in U.A.R. The thermal behaviour was studied by differential thermal analysis, thermogravimetric analysis and X-ray analysis. The results obtained showed that complete dehydration occurred at 600°C, while a new phase identified as "mullite" was formed at a temperature above 1000°C.

Carbon replicas for fractured surfaces heated to different temperatures were prepared and studied using the electron microscope. The observations were found to be in good agreement with the above results.

1. Introduction

Thermal behaviour of clays, specially that of kaolinite, is one of the important subjects in the study of kaolinite-mullite reactions. The series of reactions during which kaolinite transforms into mullite is one of the most important investigations in the entire field of ceramic technology.

Hyslop & Rooksby (1928) studied the thermal behaviour of clays using X-ray diffraction. They observed that, in the first stage, partial dehydration took place at about 500°C and metakaolin was formed. In the second stage, from 925–950°C, γ-alumina and mullite were thought to be formed. At about 1200°C, γ-alumina disappeared while mullite became more clearly defined.

Tsheischwil *et al* (1939) observed that the hexagonal morphology of kaolinite persisted into the metakaolin phase and that mullite phase was formed on specimens heated to 1200°C. Comeforo *et al* (1948) observed that mullite was formed in preferred orientation with respect to the original kaolinite crystals and mullite needles were formed sometimes in a hexagonal configuration. They also studied the rate of formation of mullite phase in some fired kaolin minerals. Direct observations carried out by Brindley & Comer (1956) using the electron micro-

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scope, showed the existence of mullite needles on the surface of kaolinite. However, electron diffraction failed to detect this mullite phase probably due to the presence of a thin film of a glassy phase coating the mullite needles.

Johns (1953) observed that poorly crystallized kaolinite developed mullite more slowly than well crystallized one. Accordingly, a time factor as well as a temperature factor should be considered. γ-alumina seemed to be always a poorly crystallized material and mullite was suggested to bear a close relation to the 1 : 1, Al_2O_3. SiO_2 minerals.

To study the thermal behaviour and phase transformation of Egyptian kaolinite, both differential thermal analysis and thermogravimetric analysis were carried out. The results obtained were confirmed by X-ray analysis. Electron microscopical studies showed variations in the surface structure of fractured specimens treated thermally for different times.

2. Experimental Procedure and Results

Differential thermal analysis was carried out to study the physical and chermical changes of Egyptian kaolinite heated to different temperatures for one and four hours.

Kaolinite was gound to pass 200 mesh and then dried. A mass of 0·5 gm of the powder was packed in one crucible where one junction of the differential thermocouple was placed. The reference inert material (calcined alumina), which does not undergo any thermal changes during the process of heating, was ground to the same size and packed in another crucible together with the second junction of the thermocouple. The block containing the two crucibles was then covered and horizontally fitted into the tube of the furnace.

The differential thermal curve is shown in figure 1. It is characterized by an endothermic reaction at 600°C and an exothermic one at 1000°C. The endothermic behaviour was due to the complete dehydration, while the exothermic reaction was due to the beginning of formation of a new phase. Moreover, ther thermal decomposition of kaolinite was studied by the method of thermogravimetric analysis. Kelley *et al* (1936) were among several investigators who adopted this method. In this method, the changes in temperature and weight were recorded automatically.

A weighed amount of kaolinite was packed in a crucible and placed inside the furnace. The variation between the temperature and loss in weight was recorded and shown in figure 2.

For further study using X-ray analysis, a portion of 200 mesh powder of kaolinite was studied at room temperature by a Philips X-rays diffractometer type PW 1050 using CuK_α radiation. Individual portions of the same powder

were heated slowly in a small platinum crucible for four hours to temperatures ranging from 500°C to 1200°C in steps of 50°C.

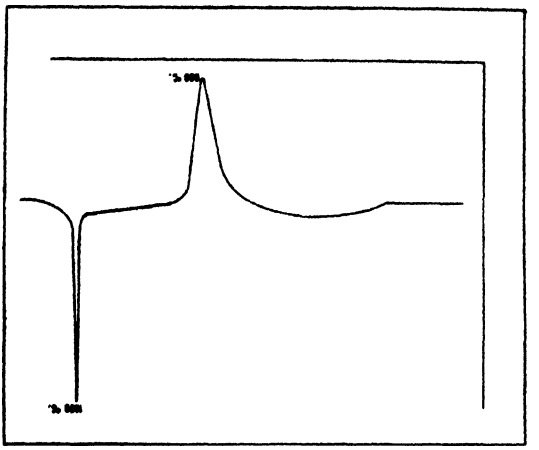

Fig. 1. Differential Thermal Analysis curve for Egyptian Kaolinite.

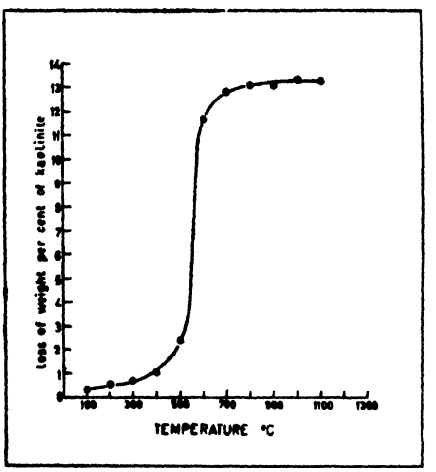

Fig. 2. Variation between the temperature and loss in weight of Egyptian Kaolinite.

The X-rays analysis of the specimen at room temperature is given in figure 3. It is characterized by intensive reflections (001) and (002) in addition to a series of lower intensity peaks. Figure 4 shows the X-ray analysis of the specimen heated to 500°C for four hours. It can be observed that a decrease in the intensity of the reflections and peaks took place. On heating the specimens to 600°C for four hours, the peaks disappeared completely as shown in figure 5. However, on heating the specimen in the range from 600°C to 900°C for the same periods, no remarkable changes were observed when compared with that of the

speimen heated at 600°C. Figure 6 shows the X-ray analysis for a specimen heated to 1000°C for four hours. It is characterized by the existence of new peaks indicating the beginning of formation of a new phase identified as "mullite". These observations are in good agreement with that of Brindley & Robinson (1946).

Fractured surfaces of kaolinite, either at room or higher temperatures, before chemical treatment or X-ray irradiation, are defined as normal surfaces.

The fractured surface of keolinite was studied using an El Mi D_2 (Carl Zeiss Jena) electron microscope. Carbon replica (Bradely 1954) for the fractured

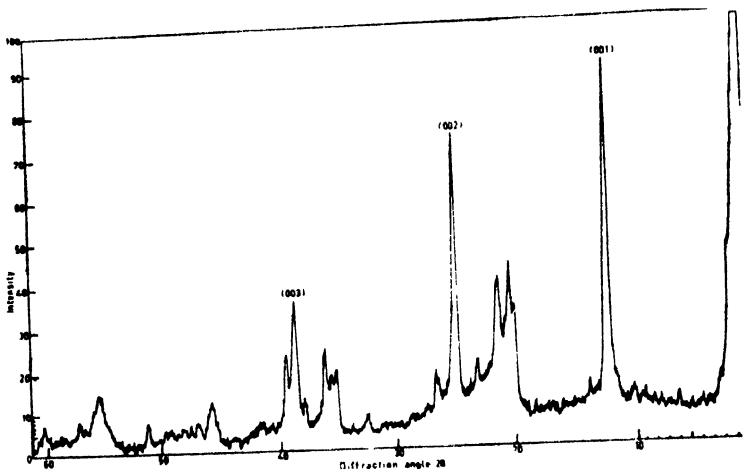

Fig. 3. X-ray diffractometer pattern of Egyptian Kaolinite at room temperature.

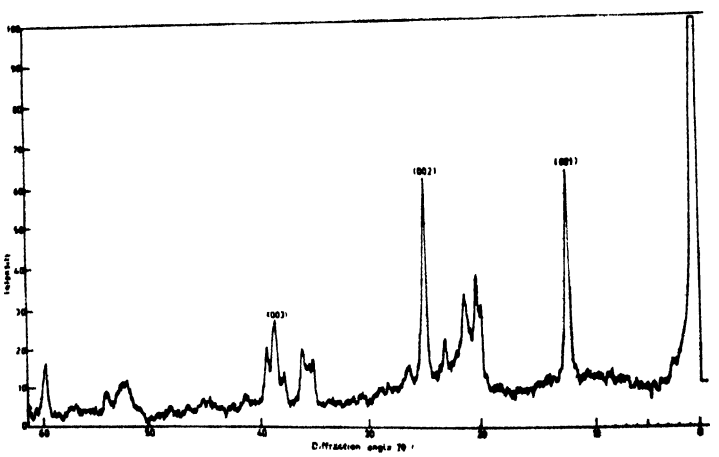

Fig 4. X-ray diffractometer pattern of the Kaolinite specimen heated to 500°C for four hours.

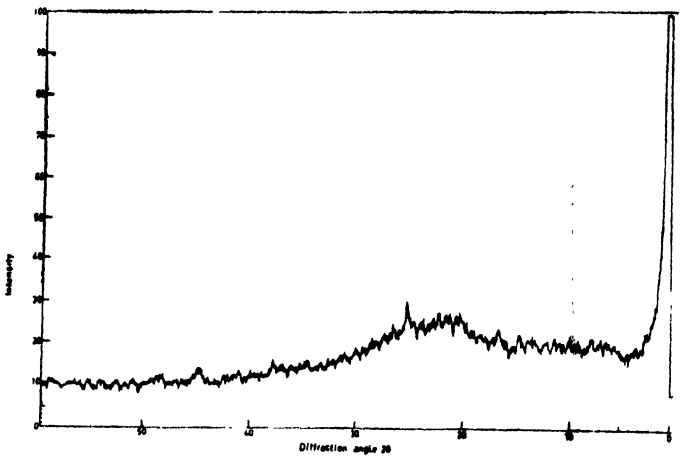

Fig. 5. X-ray diffractometer pattern of the Kaolinite specimen heated to 500°C for four hours.

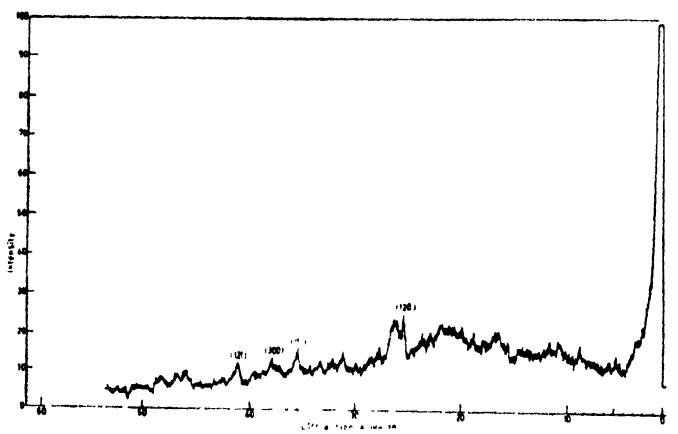

Fig. 6. X-ray diffractometer pattern of the Kaolinite specimen heated to 1000°C for four hours.

surface was found to be suitable for this investigation. This is due to its resistance to chemicals and stability against the electron beam. This was prepared using an Edward Coating Plant Model 12 E 6/586. The specimens were heated to different temperatures ranging from 500°C to 1200°C for one to four hours. The heated specimens were left to cool down slowly to the room temperature. The fractured surfaces were then replicated and investigated by the electron microscope.

Figure 7 shows the structure of the fractured surface at room temperature. It shows the existence of creaks ending with forked fractures. This may be

due to the mechanical process of fracture. Figure 8 shows the existence of randomly distributed hexagons on the surface of a specimen heated to 500°C for one hour. When the specimen was heated to 500°C for four hours, some regular tabular plates of halloysite appeared on its surface as shown in figure 9. Figure 10 shows the surface structure of a specimen heated to 600°C for one hour. Hexagons of different sizes in addition to some cubical features were observed. No new features appeared when the surface of the specimen was heated from 600 to 900°C for the same times. When the specimen was heated above 900°C for four hours, the size of the pre-existing hexagons increased and some cubes with well defined edges appeared. Moreover, these features were arranged in steps as shown in figure 11. However, needle shaped particle, surrounding the sides of the pre-existing hexagons, appeared on the surface of a specimen heated to 1100°C for four hours as shown in figure 12. These needles indicate the formation of a new phase identified by X-ray diffraction as "mullite". When the specimen was further heated to 1200°C for same times, the needles appeared to be oriented and aggregated.

3. Discussion

The differential thermal analysis of kaolinite showed that the dehydration of the sample began at 500°C and was completed at 600°C. This was characterized by an endothermic peak. While an exothermic peak was obtained at 1000°C indicating the beginning of the formation of a phase identified by X-ray diffraction as "mullite".

The results obtained from the thermogravimetric analysis were in good agreement with the above ones.

X-ray diffraction analysis for a specimen at room temperature showed intense reflection peaks (001) and (002) in addition to group of lines of lower intensity. When the specimen was heated to 500°C, a decrease in intensity took place. This indicated the beginning of dehydration. Complete dehydration, characterized by the disappearance of the above reflection peaks and group of lines, occurred when the specimen was heated to 600°C. Furthermore, when the specimen was heated to 1000°C, new peaks appeared indicating that beginning of formation of a phase identified as "mullite".

For the above investigation, the samples were ground to pass 200 mesh. This particle size was found to be in favour of phase transformation at low temperatures.

Moreover, carbon replicas of fractured surfaces of kaolinite at different temperatures were prepared and then studied using the electron microscope. Cracks, which may be due to the fracture process, appeared on the surface of the specimen at room temperature. Heating the specimen to 500°C, halloysite

Fig. 7. Electron micrograph of the fractured surface of Kaolinite specimen at room temporature.

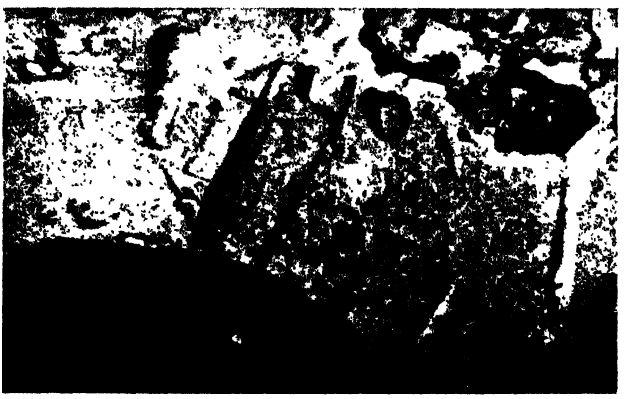

Fig. 8. Electron micrograph of the fractured surface of Kaolinite specimen heated to 500°C for one hour.

Fig. 9. Electron micrograph of the fractured surface of Kaolinite specimen heated to 500°C for four hours.

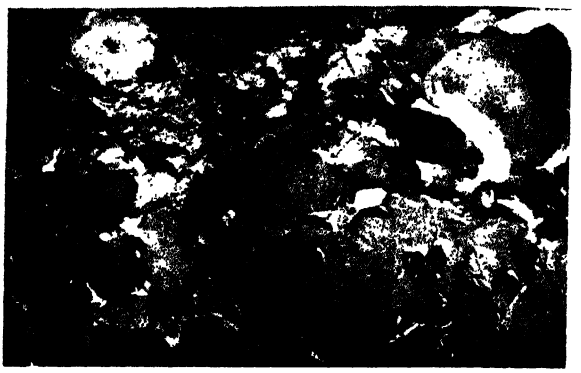

Fig. 10. Electron micrograph of the fractured surface of Kaolinite specimen heated to 600°C for one hour.

Fig. 11. Electron micrograph of the fractured surface of Kaolinite specimen heated to above 900°C for four hours.

Fig. 12. Electron micrograph of the fractured surface of Kaolinite specimen heated to 1100°C for four hours.

tubes as well as hexagons were observed. According to Taylor (1964), these features indicate the beginning of dehydration of the specimen. The change of these features into cubes when the specimen was heated to 600°C indicates the complete dehydration of the specimen. This was confirmed since no further changes on the surface were observed when the specimen was heated from 600°C to 900°C.

An increase in size of the pre-existing hexagons and formation of cubes with well defined edges for a specimen heated to above 900°C were observed. These features may be due to the formation of γ-alumina. This was in good agreement with the results obtained by Hyslop & Rooksby (1928) who showed that γ-alumina began to be formed in the range from 925°C to 950°C.

However, needles were observed on the surface of the specimen when heated to 1000°C. This was taken to indicate the beginning of formation of a phase identified as "mullite".

4. Conclusion

It can be concluded that the electron microscopical observations for normal fractured surfaces are in good agreement with the measurements of both differential thermal analysis and X-ray analysis. Therefore, the thermal behaviour and phase transformation of chemically etched surface after being heated, as well as X-ray irradiated surfaces can be studied using the electron microscope alone.

Acknowledgement

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